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A procedure to determine the optimum imaging parameters for atomic/molecular resolution frequency modulation atomic force microscopy

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We propose a general procedure to determine the optimum imaging parameters (spring constant and oscillation amplitude) to obtain the optimum resolution in frequency modulation atomic force microscopy. We calculated the effective signal-to-noise ratio for various spring constants and oscillation amplitudes, based on the measurement of frequency shift and energy dissipation versus tip-sample distance curves, to find the optimum. We applied this procedure for imaging a lead phthalocyanine (PbPc) thin film on a $MoS_2(0001)$ substrate, and found that the optimum parameters were about 5 N/m and 20 nm, respectively. An improved signal-to-noise ratio was attained in a preliminary experiment using parameters which were close to the calculated optimum.
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I. INTRODUCTION

Scanning probe microscopy (SPM) is an important research tool in the fields of nanotechnology and nanoscience. Among the various SPMs, frequency modulation atomic force microscopy[1] (FM-AFM) is becoming a very powerful tool for imaging individual atoms or molecules on various surfaces, such as semiconductors, metals, and organic materials.[2] Recent studies have shown that the lateral resolution of FM-AFM on a Si(111)-7×7 surface can be improved by oscillating a force sensor with a very high spring constant (>1000 N/m) at a very small amplitude (<1 nm).[3,4] We recently employed a stiff Si cantilever, whose spring constant was about 700 N/m, for imaging lead phthalocyanine (PbPc) thin films on a $MoS_2(0001)$ substrate with an oscillation amplitude of about 1 nm;[5] however, the lateral resolution of the image was not greatly improved. A possible reason for this was that we could not sufficiently reduce the oscillation amplitude because of the large dissipative interaction force.[6–8]

Now we realize that using a very stiff cantilever may not always improve the lateral resolution in FM-AFM, especially in a case where the dissipative interaction is large. Previous discussions on optimum imaging parameters were made based on the calculation of the signal-to-noise ratio for various model potentials with small dissipative interactions.[3] In this paper, we propose a procedure to determine the optimum imaging parameters (spring constant and oscillation amplitude) for obtaining atomic or molecular resolution by FM-AFM, based on the measurement of the frequency shift and energy dissipation versus tip-sample distance curves. Since the procedure does not require the assumption of model potentials, it is applicable for imaging any samples.

II. OUTLINE OF PROCEDURE

The procedure we propose is as follows. First, we perform atomic or molecular resolution imaging using an initial cantilever with a typical oscillation amplitude, and measure the frequency shift and energy dissipation versus tip-sample distance curves. From these curves we determine the minimum distance (d_{min}) at which the tip can travel without instability in the self-oscillations, which is determined by either criteria described below. Second, we determine an effective frequency signal as the difference between the frequency shift on top of the atom/molecule and in the gap between the atoms/molecules at d_{min}, as shown in Fig. 1. Then we compute the effective frequency signal for various spring constants and amplitudes from the measured frequency shift curves. Finally, we determine an effective signal-to-noise ratio (ESNR) for the various parameters as the ratio of the effective frequency shift to an estimated amount of frequency noise.

The minimum distance d_{min} is limited by either of the following criteria.[3] The first criterion is that the restoring force of the cantilever (kA), which is a product of the spring constant (k) and oscillation amplitude (A), should be larger than the tip-sample interaction force (F_{ts}), otherwise the tip will be pulled into the surface. Another criterion is that the energy dissipation of the cantilever (ΔE), induced by the tip-sample dissipative interaction, should be less than a certain value which is proportional to the kinetic energy of the cantilever ($E_{cl}=kA^2/2$). The maximum energy dissipation (ΔE_{max}) at which the cantilever maintains stable oscillation depends on the bandwidth of the amplitude regulator circuit;

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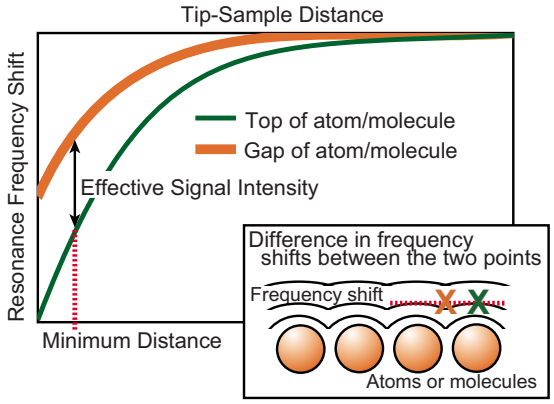

FIG. 1. (Color online) Schematic of frequency shift curves in atomic/molecular resolution frequency modulation atomic force microscopy. We defined the effective signal intensity as the difference between the frequency shift on top of the atom/molecule and in the gap between the atoms/molecules at the minimum distance (d_{min}) at which the tip can be moved stably.

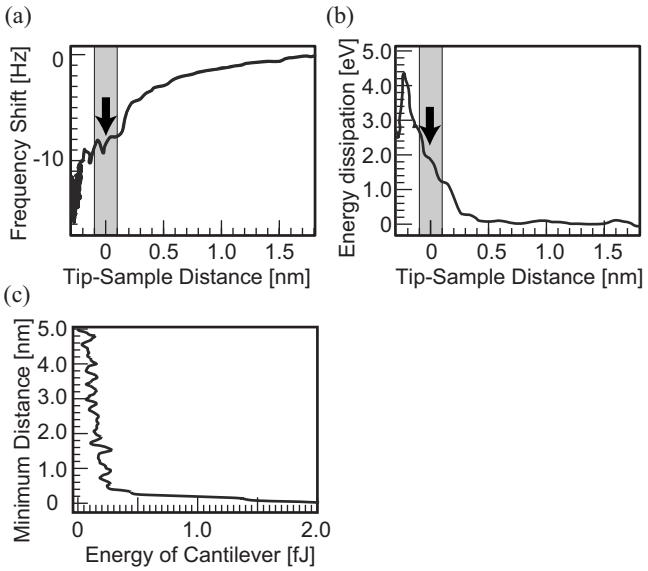

FIG. 2. (a) Frequency shift vs tip-sample distance curve measured on PbPc thin film using initial parameters (k=40 N/m, A=10 nm). (b) Energy dissipation vs tip-sample distance curve measured simultaneously with (a). (c) Plot of d_{min} as a function of the kinetic energy of the oscillating cantilever. Note that d_{min} increases as the kinetic energy decreases.

however, it is almost the same order as the energy loss per cycle of a freely oscillating cantilever, $\pi kA^2/Q$, where Q is a mechanical Q-factor. For stable operation of the FM-AFM, these two criteria, $F_{ts}<kA$ and $\Delta E<\Delta E_{max}$, should always be met during operation.

Note that the cantilever parameters, such as the mechanical Q-factor and the resonance frequency (f_0), also affect the ESNR. However, they strongly depend on the operating conditions and a dimension of the cantilever, and the ESNR undoubtedly increases as both parameters increase more. Therefore, in this study, we limited the parameters of concern to the spring constant and oscillation amplitude.

III. APPLICATION EXAMPLE

In the following section, we describe the details of the procedure as we determine the optimum parameters for imaging an organic thin film. The sample used was a PbPc thin film on a MoS_2(0001) surface. We deposited PbPc molecules on the MoS_2 substrate in an ultrahigh vacuum chamber whose base pressure was less than 10^{-7} Pa and imaged the sample surface, without exposing the sample to air, using a commercially available AFM apparatus (JEOL:JAFM-4500XT). Several optical components and electronic devices, such as a laser diode, a collimator, a focusing lens, and preamplifiers, were replaced to achieve a low deflection sensor noise.[9]

A home-built FM controller[10] was used to oscillate the cantilever at its resonant frequency and to detect a frequency shift. We also used a home-built AFM controller to measure curves of the frequency shift and energy dissipation versus tip-sample distance and to obtain the two-dimensional frequency shift map. The control software was coded by LABVIEW (National Instruments Corp.), which runs on a control system (PXI-8196) with a field-programmable gate array card (PXI-7833R). We used a Si cantilever (Nanosensors: NCH) with a nominal spring constant of 40 N/m as the initial cantilever. The oscillation amplitude was kept at 10 nm peak-to-zero, which is typical for imaging molecules at molecular resolution with this cantilever.[6] Since Q and f_0 of the NCH cantilever in vacuum were about 10 000 and 300 kHz, respectively, we used these values as fixed parameters in the following calculations. Therefore, the kinetic energy of the cantilever in the experiment was 2×10^{-15} J and the intrinsic energy loss per cycle was 1.3×10^{-18} J (7.8 eV).

First, we measured the curves of frequency shift and the energy dissipation versus tip-sample distance using the reference sweep method[11] on PbPc thin film, as shown in Figs. 2(a) and 2(b), respectively. Both curves show fluctuations when the tip travels to the distance range indicated by the shaded area. The first criterion mentioned above ($F_{ts}<kA$) was still met in this range because kA was 40 nN and F_{ts} was less than 0.3 nN, as shown later in Fig. 3(b). Therefore, we assume that the oscillation fluctuation occurred because of the dissipative interaction (the second criterion) in this case. We chose d_{min} for the initial conditions in this range, as indicated by an arrow, and set it at 0 nm. It should be mentioned that the error range in the calculated optimum parameters was up to about 20%, if d_{min} was chosen within the shaded area.

The cantilever oscillation became unstable when the energy dissipation due to the tip-sample interaction reached 0.3×10^{-18} J (1.9 eV), which is on the same order as the intrinsic energy loss of the cantilever per cycle. This is probably because the fluctuation of molecules is induced by the tip-sample interaction force, and thus the energy dissipation of the cantilever on molecules is typically high compared to that on inorganic samples.[12] If E_{cl} decreases, d_{min}, where ΔE reaches ΔE_{max}, increases. Therefore, we can plot d_{min} as a function of the kinetic energy of the oscillating cantilever, as shown in Fig. 2(c), by assuming that the acceptable dissipation energy decreases in proportion to the kinetic energy, and thus d_{min} increases accordingly.

Second, we obtained a two-dimensional frequency shift map of the PbPc thin film, as shown in Fig. 3(a). Figure 3(b)

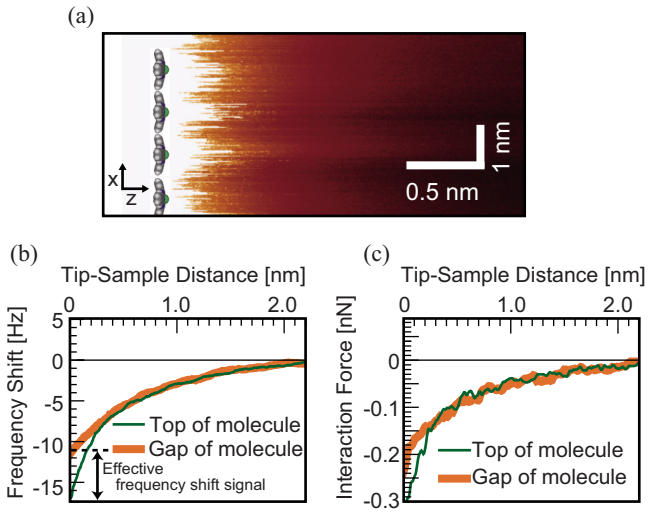

FIG. 3. (Color online) (a) Two-dimensional frequency shift map on PbPc thin film measured using initial parameters (k=40 N/m, A=10 nm). (b) Frequency shift vs tip-sample distance curves on top of PbPc molecule and in the gap between the PbPc molecule extracted from (a). (c) Force vs tip-sample distance curves converted from (b) using Sader's formula (Ref. 13).

shows a pair of frequency shift versus tip-sample distance curves measured on top of the molecule and at the gap between the molecules, extracted from Fig. 3(a). The effective frequency shift signal under the initial conditions was measured as 6 Hz, as shown in the figure. To calculate the ESNR for all combinations of spring constants and oscillation amplitudes, we needed to compute this pair of frequency shift curves for those parameters. We converted a pair of frequency shift curves to corresponding force curves,[13] as shown in Fig. 3(c). Then we computed frequency shift curves for all combinations of spring constants and oscillation amplitudes using the following formula:[14]

$$\Delta f(z) = \frac{f_0}{\pi k A}\int_{-1}^{1} F_{\mathrm{ts}}[z + A(1+\cos 2\pi f_0 t)]\frac{u}{\sqrt{1-u^2}}du, \tag{1}$$

where z and u are the tip-sample distance and an integrating variable (u=cos $\omega_0 t$), respectively. The effective frequency shift signals were determined by the frequency shift difference at d_{min} for each combination of parameters.

Finally, we estimated the frequency noise (δf) for all the parameters. The frequency noise of the high-Q cantilever is given by the following equation:[15]

$$\delta f(k,A) = \sqrt{\frac{f_0 k_{\mathrm{B}} T B}{\pi k Q^2} + \frac{2{n_{\mathrm{ds}}}^2 B^3}{3A^2}}, \tag{2}$$

where k_{B}, T, B, and n_{ds} are the Boltzmann constant, temperature, measurement bandwidth, and noise-equivalent deflection density of the deflection sensor, respectively. We fixed B and n_{ds} to typical experimental parameters, such as B=1000 Hz and n_{ds}=30 fm/$\sqrt{\mathrm{Hz}}$, respectively. For example, the ESNR for the initial set of parameters was calculated as 47.

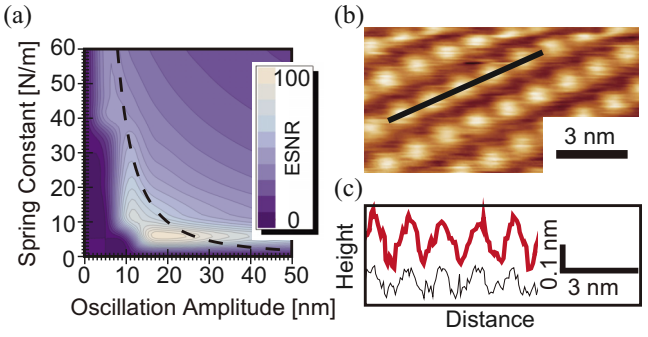

FIG. 4. (Color online) (a) ESNR for molecular resolution imaging of PbPc thin film using FM-AFM, calculated for various spring constants and oscillation amplitudes. The optimum parameters with the highest ESNR (light contrast in the figure) were found around k=5 N/m and A=20 nm. (b) Topographic image of PbPc thin film measured using experimental parameters close to the calculated optimum conditions (k=7 N/m and A=15 nm). (c) Cross-sectional profile measured on the line indicated in (b) (thick curve) and that measured on the image obtained using the initial cantilever (thin curve) (Ref. 5).

The ESNR for molecular resolution imaging on PbPc film calculated for all combinations of parameters was plotted two-dimensionally in Fig. 4(a). The light contrast in the plot represents the parameters with a high ESNR. The optimum spring constant and oscillation amplitude were found at around 5 N/m and 20 nm, respectively. The parameters on the black dotted curve correspond to imaging conditions with the same E_{cl} as that of the initial conditions (2×10^{-15} J). The ESNR for the parameters with higher E_{cl} was calculated by extrapolating the frequency shift and energy dissipation curves for $d_{\mathrm{min}}<0$, using inverse power law functions and linear functions, respectively. The maximum ESNR was found in the range where E_{cl} was smaller than that in the initial conditions. It should be noted that no extrapolation is necessary to find the optimum parameters if one performs the experiment with a sufficiently large E_{cl}.

We performed FM-AFM imaging using parameters which are close to the optimum. Since it is difficult to use a cantilever whose spring constant exactly matches the optimum (5 N/m), we used a Si cantilever (Nanosensors: NCST) with a nominal spring constant of 7 N/m, which is close to the optimum. The resonance frequency was 160 kHz. Figure 4(b) shows a preliminary experimental result using the NCST cantilever oscillated at an amplitude of about 15 nm peak-to-zero. Figure 4(c) shows cross-sectional profiles measured on the line indicated in Fig. 4(b) (thick curve) and that of the best image obtained using the NCH cantilevers with the initial parameters (thin curve).[5] These images were acquired at almost the same normalized frequency shift [2.3 fN$\sqrt{\mathrm{m}}$ for Fig. 4(a) and 2.5 fN$\sqrt{\mathrm{m}}$ for the image in Ref. 5]. We found that the background noise in the profile taken from Fig. 4(a) was less, whereas the corrugation amplitudes were almost the same.

IV. CONCLUSIONS

We proposed a procedure to determine the optimum imaging parameters, the spring constant, and oscillation amplitude for atomic/molecular resolution FM-AFM. Using this procedure, one can determine the optimum parameters on

any surface, even if the tip-sample dissipative interaction is large. We calculated the effective signal-to-noise ratio on a PbPc thin film as a practical sample, and we found that the optimum parameters were about 5 N/m and 20 nm. We also performed molecular resolution imaging on a PbPc thin film using imaging parameters, which were close to the calculated optimum parameters, and we confirmed that the resolution of the image was improved compared to that obtained under conventional conditions.

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